

In-Situ NMR Study of Activated Peroxide Decontamination of ^{13}C -enriched HD

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Background

Base-activated hydrogen peroxide formulations are under development as broad spectrum decontaminants for chemical and biological weapons. In the decontamination of nerve agents such as VX and GD, these formulations produce the perhydrolysis products ethyl methylphosphonic acid (EMPA) and pinacolyl methylphosphonic acid (GD acid), respectively. The decontamination of distilled mustard (HD) produces a more complex mixture of products, which are not readily characterizable by any single analytical technique.



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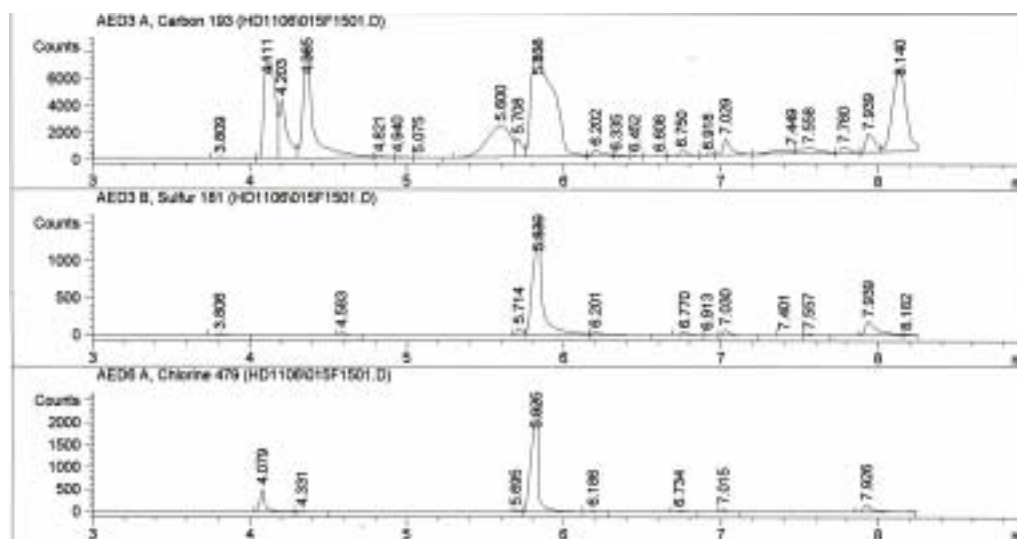
Analytical Results

Initial GC-MS analysis of reaction masses produced by base-activated peroxide decontamination of HD identified bis(2-chloroethyl) sulfoxide (mustard sulfoxide) as a major product. However, in-situ NMR analysis of ^{13}C -enriched HD decontamination in base-activated peroxide formulations shows the formation of additional reaction products, and substantial change in the distribution of reaction products in the first 24 hours after decontamination. ^{13}C -enrichment allows the HD products to be clearly distinguished from the components of the decontamination formulation, and facilitates identification of the reaction products. The identification of dehydrohalogenated and oxidized HD products will be discussed.

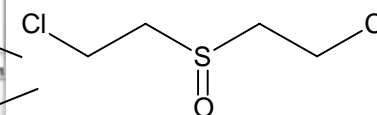
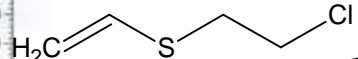
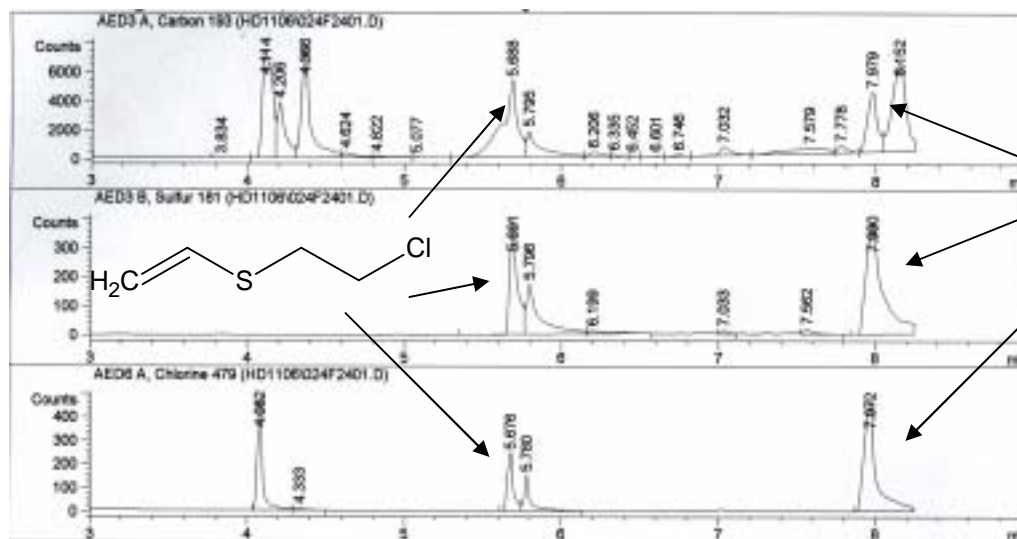


Preliminary Identification of Initial HD Degradation Products in MDF-1 by GC-AED

T = 1 min.



T = 60 min.

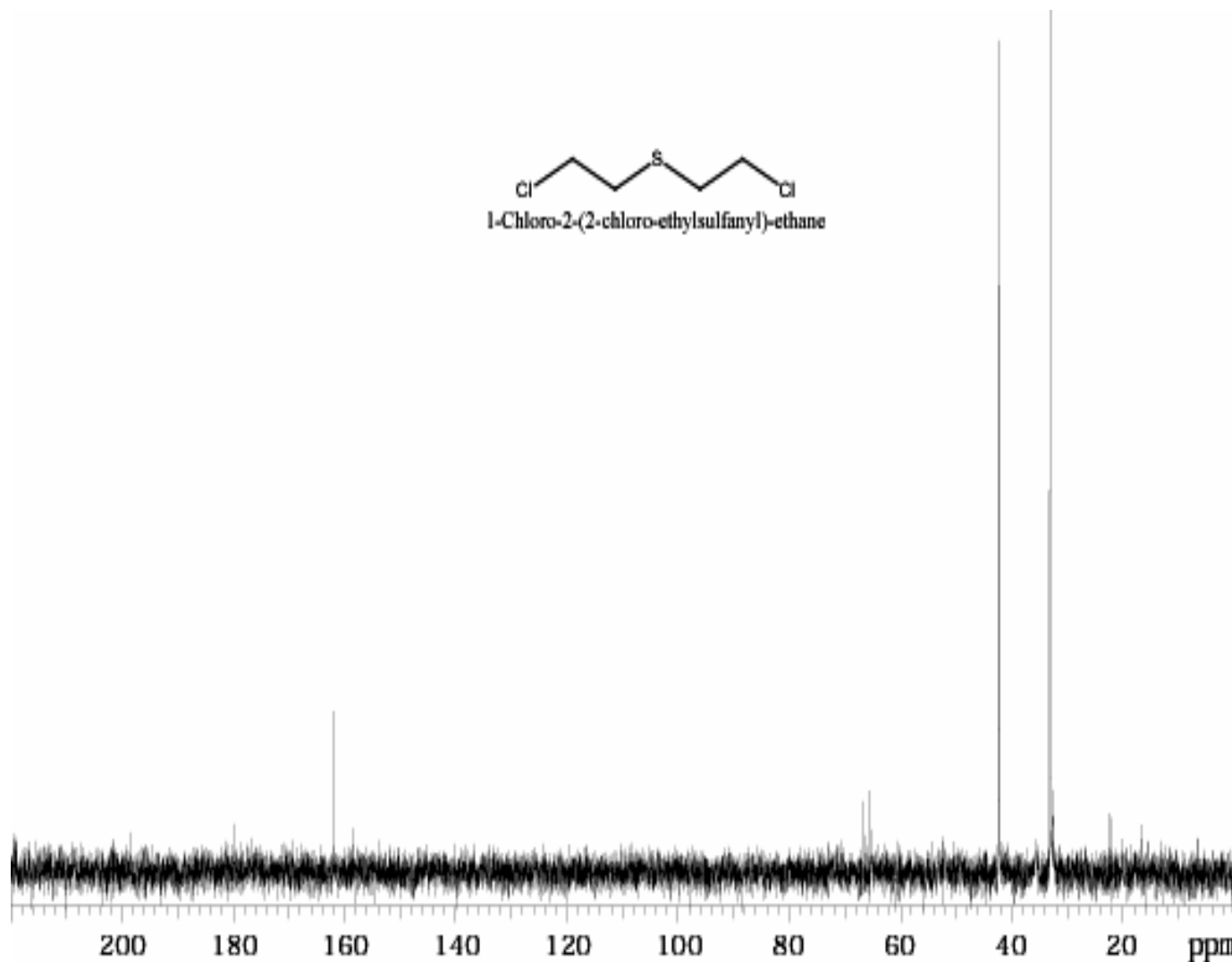
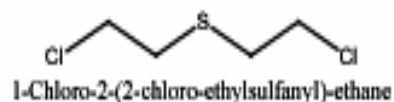


Experimental

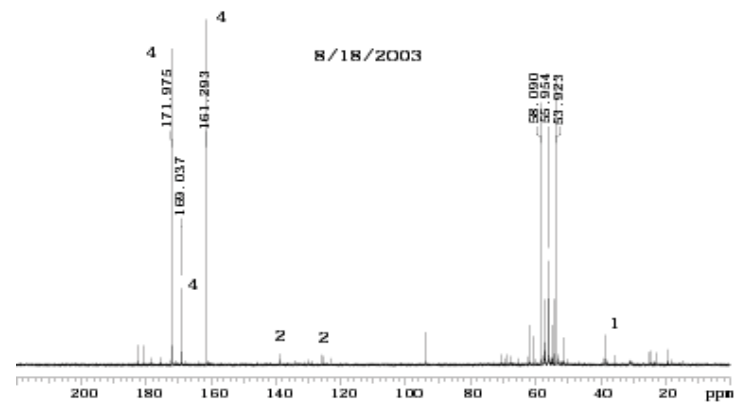
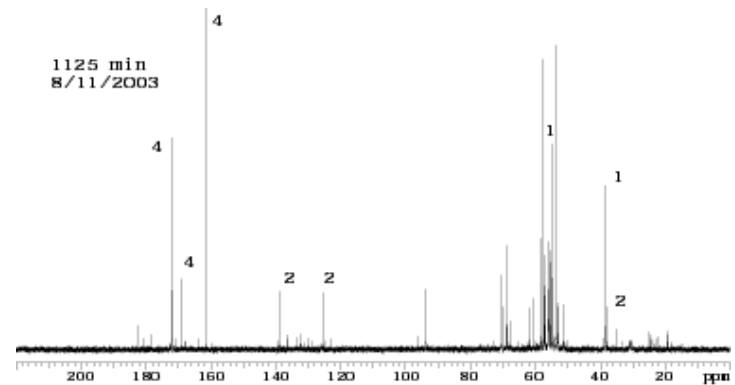
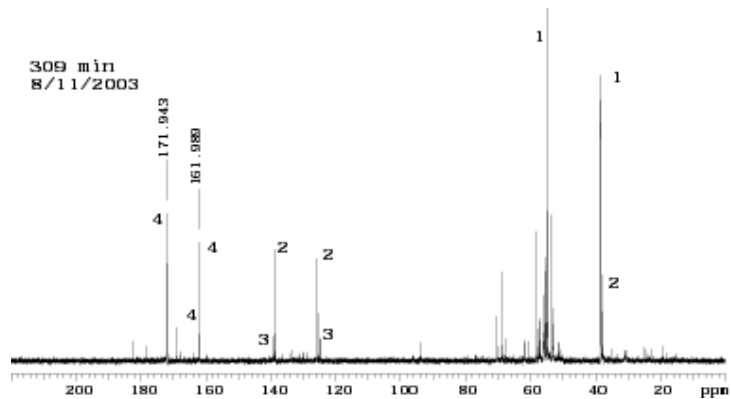
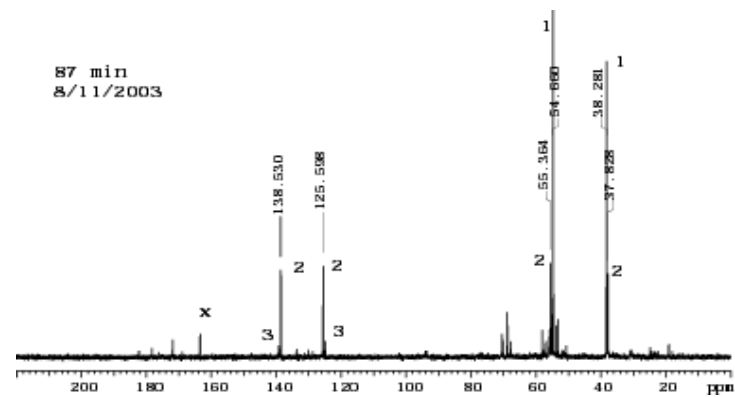
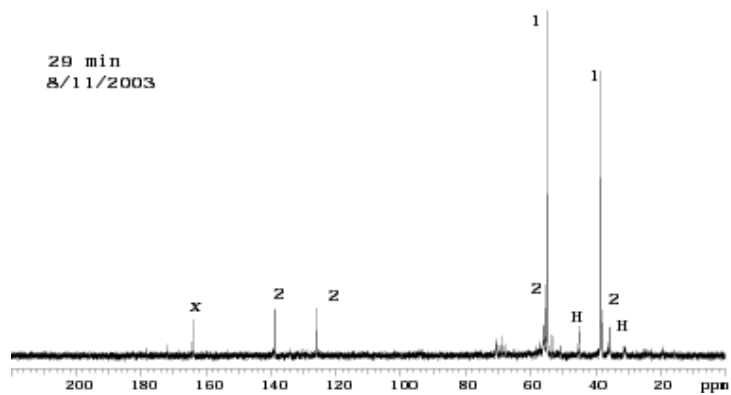
- In-situ NMR experiments performed with 20mg of ^{13}C -enriched HD in 1 gram of decon. solution in 5mm NMR tube
- Agent operations carried in accordance with Surety SOP CR8-0SP035, The NMR Experiment for Liquids and Solids
- Tube maintained at 25 °C
- Degradation of mustard recorded by ^{13}C NMR analysis at various time intervals.
- NMR spectra acquired on Varian 600 MHz narrow bore NMR, E3300, Rm 2
- 5 mm Broadband, triple axis gradient PFG probe
- Gradient shimming used for expedited shimming on non-deuterated samples



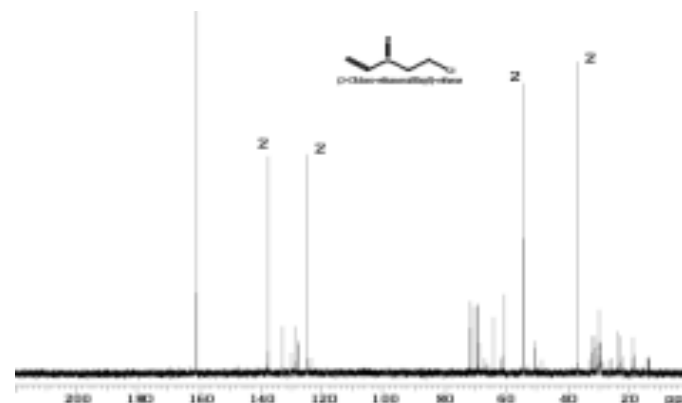
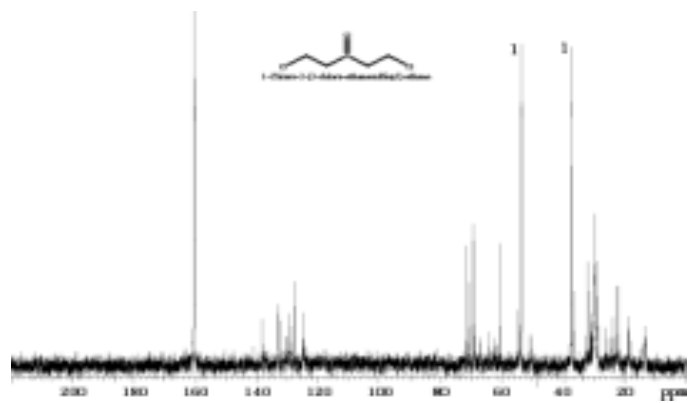
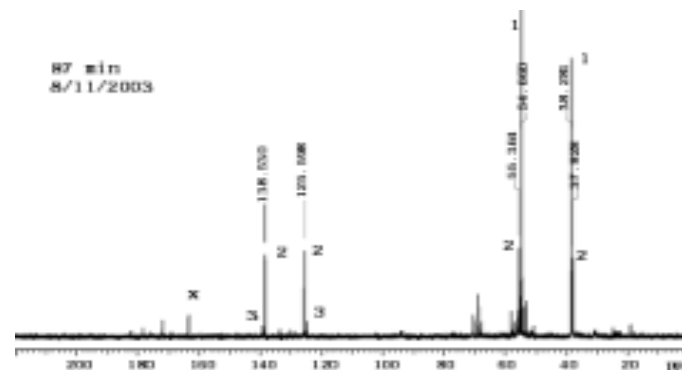
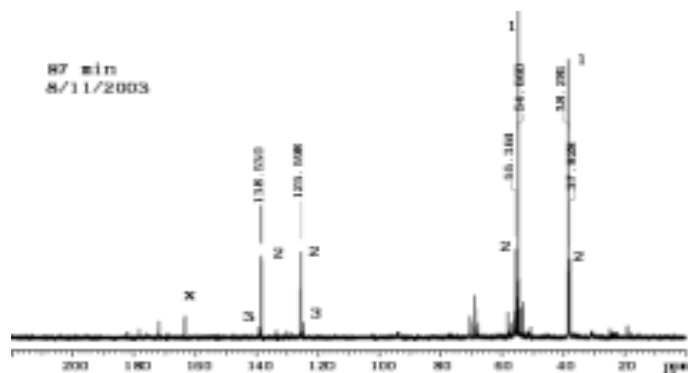
Initial Time Point ^{13}C NMR Spectrum of ^{13}C -enriched HD in MDF-1, Showing HD Methylene Peaks @ 32.5 and 31.5 ppm



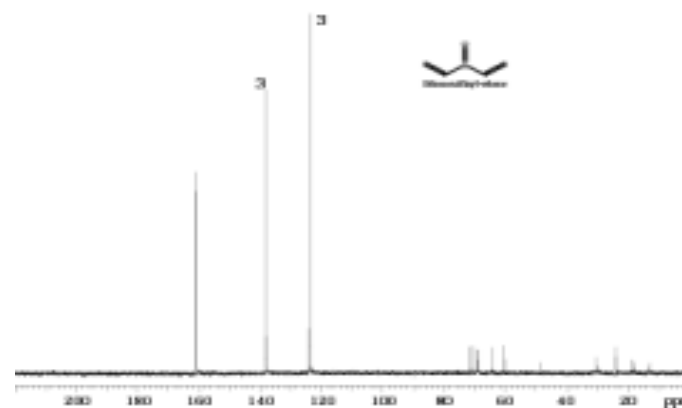
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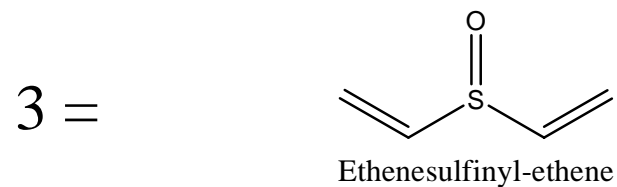
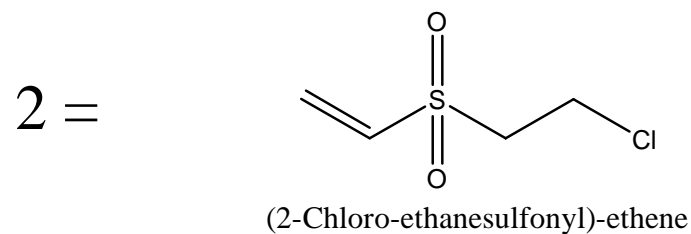
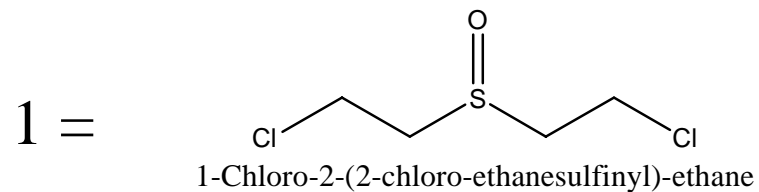
^{13}C -enriched HD in MDF1
@ RT vs. time



Comparisons ^{13}C NMR spectra of
 ^{13}C -enriched HD in MDF1 @ RT to
reference compounds



Tentative assignments for the MDF-1 experiment



4 = unknown carbonyl signals



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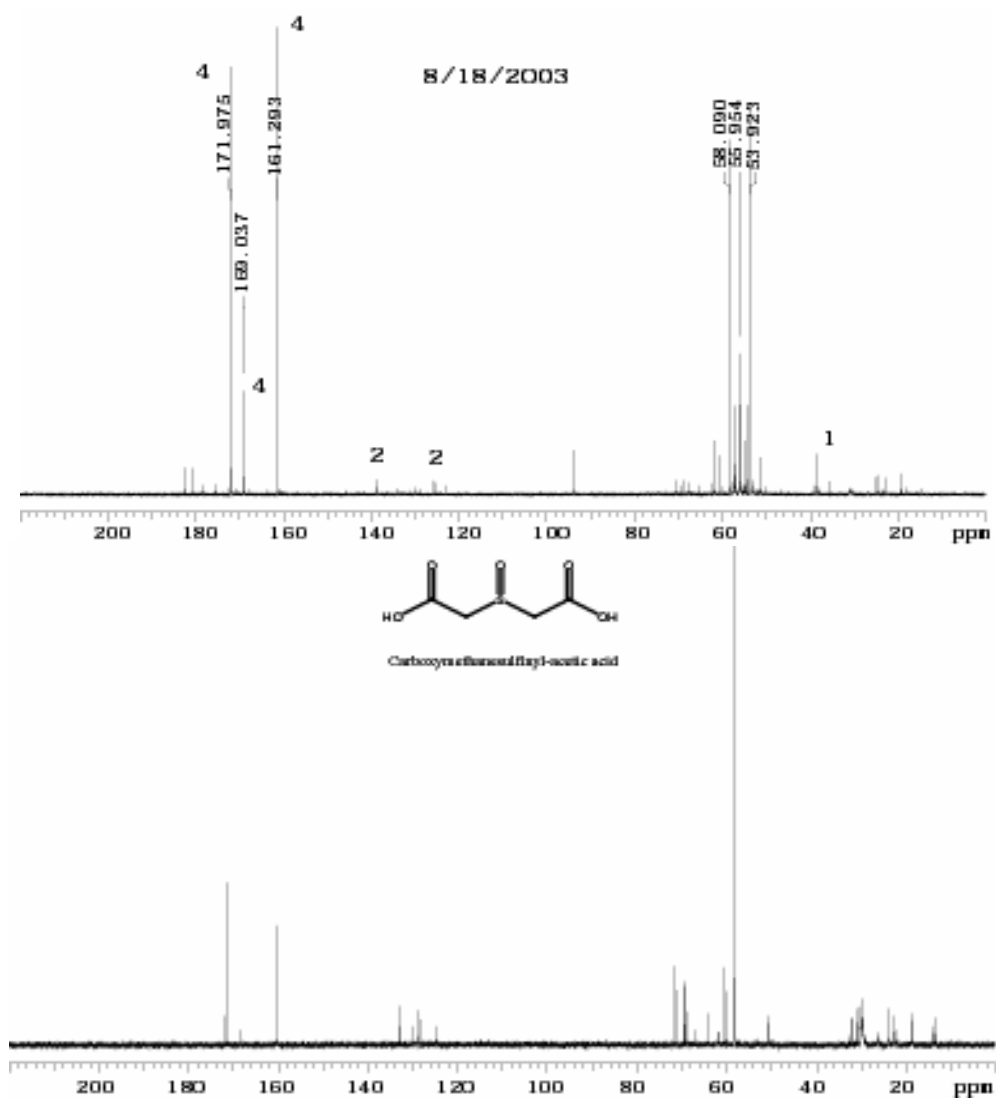
Initial Results

1. First immediate products are the mustard sulfoxide (HDO, 1) and 2-chloroethyl vinylsulfoxide (2)
2. By 87 min can see small signals for the divinyl sulfoxide (3) and small signals that represent the carbonyl species (4)
3. By 1125 minutes (18 hrs. 45 min) the carbonyl species (4) dominate and further resolve one week later (8/18/2003)
4. Preliminary standards synthesis and 2-D NMR analyses indicate that species (4) is a carboxylic acid derivative of HD sulfoxide



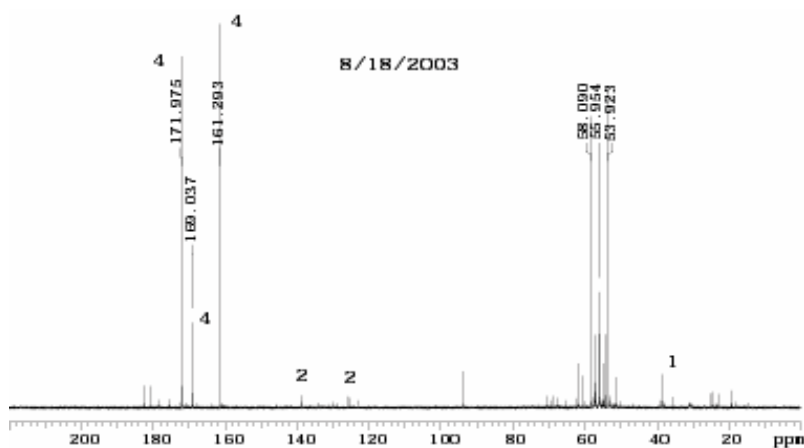
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Reference Sample of Dicarboxylic Acid Derivative of HD Sulfoxide Matches Two Major Product Peaks in MDF-1 Reaction Mass

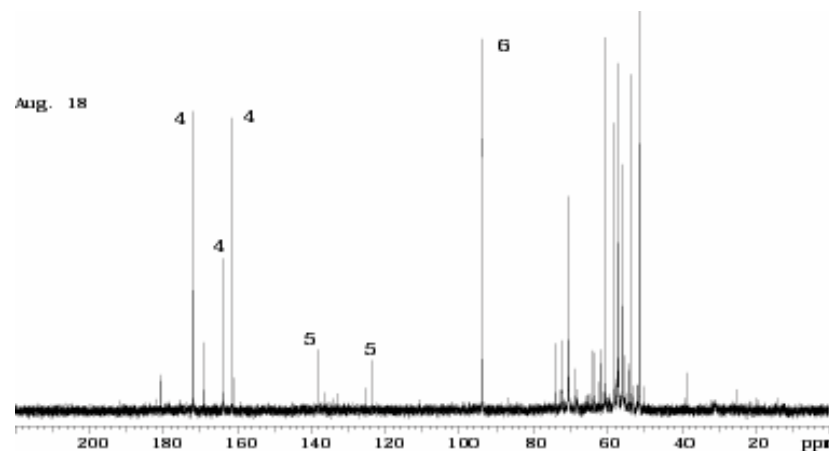


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The ^{13}C NMR Spectra ^{13}C -enriched HD in MDF-1 and in EFT-2
After 7 Days at RT Indicate at Least One Common
Carboxylic Acid Product, but the EFT Reaction Mass Contains
at Least Two Additional, Novel Products



MDF-1



EFT-2



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Table 1: Toxic Properties of HD, HDO, HDO₂, 2-Chloroethylvinyl sulfoxide and Divinylsulfoxide

	Toxicity, LD ₅₀ (mouse, mg/kg)	Vesicant Action	Relative Hydrolysis Rate
HD	125 ^a ; 8.6 ^b	most irritating ^c ; severe ^d	Fast (50% in 10 min, 20°C) ^c
HDO	125 ^a	scarcely irritating ^c ; none ^d	Not hydrolyzed, even at 100°C ^c
HDO ₂	105 ^a ; 50 ^b	slightly less than HD ^c ; severe ^d	Slow (55.9% in 150 min, 22°C) ^c
2-chloroethyl vinyl sulfoxide	100 (LD _{LO}) ^e	Not available	Not available
Divinyl sulfoxide	50 (LD _{LO}) ^e	Not available	Not available

^aSubcutaneous, reference 10. ^bIntravenous, reference 12. ^cReference 10. ^dReference 11.

^e Oral, Reference 13.

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